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Investigation of Electronic Corrosion at Device Level

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This work presents device level testing of a lead free soldered electronic device tested with bias on under cyclic humidity conditions in a climatic chamber. Besides severe temperature and humidity during testing some devices were deliberately contaminated before testing. Contaminants investigated are ionic or airborne contaminants likely to be introduced by production or service conditions. The effect of changes in processing parameters as a result of production shift to lead free solder (e.g. higher soldering temperature) has also been investigated. Analysis have shown that one printed circuit board assembly (PCBA) in the device is more prone to corrosion reliability and this was further analysed using thermography to detect areas that have high risk of condensation due to lower temperature under working condition. Tested PCBAs are subjected to detailed investigation before and after testing using high resolution photography, detailed optical microscopy and SEM/EDS.

Introduction

The miniaturization of electronic systems and the increase in their usage has augmented the risk of corrosion in electronics devices. Problems are compounded by the fact that these systems are built by multi-material combinations and reasons such as process related residues, bias voltage, and unpredictable user environment. The demand for miniaturized devices has resulted in higher density packing with reduction in component size, closer spacing, and thinner metallic parts. Material loss of the order of nano-grams can cause reliability problems (1) in such cases especially with the present day use of electronics in all walks of life. Over the last 10 years, the pattern of electronics usage has been considerably changed due to the increased use of electronically controlled machines, use of more electronics in the transportation sector, and rapid growth in consumer electronics. The consumer electronics sector is one area where the user environment is highly unpredictable. One such example is the wide-spread use of cell phones (2). Global manufacturing net-works with unpredictable component supply chain and unclean components is another factor contributing to corrosion reliability.

Miniaturization at all levels is one of the key factors reducing corrosion reliability. Over the last 10 years, size of the electronics has been reduced by more than 70%. For flip chip ICs, miniaturization amounts to $\sim 90\%$. The closer spacing increases the electric field ($E = V/d$), which makes corrosion cell formation easy during local condensation under humid environments. The average size of dew droplet formation on surfaces at different temperatures varies from 20 – 50 μm at about 50% RH (3). Hence smaller distance on PCBAs makes it easy for the local electrochemical cell to form. Condensing may result in

functional failures, caused by corrosion, flash over or leakage currents. Some of the failures will be permanent and other may disappear, as the condensed water evaporates.

The term local condensing is used where a small part of the product is still cold enough to form condensation. Thermal heavy components and air flow are important factors in formation of local condensation. Also the ability to evaporate condensed water is important for a product to be able to survive local condensing. Therefore, high levels of design factors are involved in products response to humidity and condensation.

Corrosion problems experienced by electronic systems can be generalized as due to the following key factors. These are miniaturization together with: (i) unfavorable material combinations, (ii) DC or AC electric field applied to the system in use, (iii) process related ionic residues on the PCBA surface, and (iv) service related factors such as high humidity, gases, aggressive ions, dust, etc. Service related as well as process related residues or contamination left on a PCBA surface is a key factor accelerating corrosion. Figure 1 sketches the variety of factors likely to influence electronic corrosion.

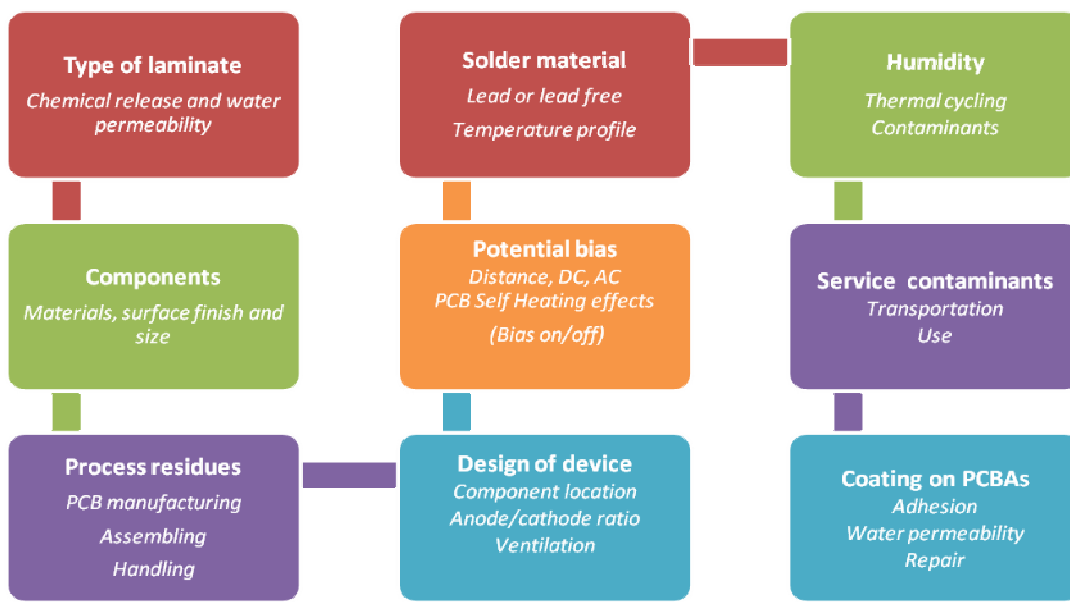


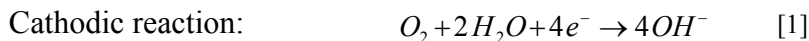
Figure 1. Overview of reliability threats in the life time of an electronic product.

Presently the mechanistic knowledge on electronic corrosion is limited, especially the relation to synergistic effects of process related residues and contamination coming from service conditions.

The probability of seeing condensation of a moisture layer large enough to bridge positively and negatively charged conductors on a PCBA increases with the decreasing distance between components, and this will constitute a corrosion cell formation. Corrosion of metals (points on PCBA) connected by water layer can occur as a result of the applied potential or due to galvanic corrosion if dissimilar materials are coupled. The incorporation of many different and very complex components in electronic circuits adds to this reliability threat. The metallic materials used on a PCBA often consist of a multitude of materials, often selected for their electrical, mechanical, or magnetic

properties rather than for their corrosion-related performance. This increases the risk for electrolytic migration or galvanic corrosion due to connections introduced through the moisture layer or condensed water layer.

The basic corrosion process taking place at the anode (positive electrode) and cathode (negative electrode) can be described by the following reactions:



The cathode reaction is the reduction of oxygen, while the reaction at the anode will dissolve the metal constituting the electrode and possibly cause failure after an extended time of application. Due to the applied bias potential, which often greatly exceeds the equilibrium potentials of the metals, and the resulting high electric field between closely spaced conductors, the corrosion mechanism in electronics are often more complex and diverse than expressed by the two above equations. Depending on the magnitude of applied potential, other reactions can contribute to the anodic/cathodic reactivity at the electrodes, and dissolved ionic contamination in the moisture can in this regard have large effects on the corrosion behaviour of the system by reacting with metal-ions or take part in the electrode reactions. The transfer of charge through a medium and at the electrodes is necessary for the corrosion reactions to be sustained, and the magnitude of this leakage current will depend on the on the aggressiveness and conductivity of the medium. Three basic factors must be present and interact as a prerequisite for a substantial leakage current to flow between conductors, and they are:

- A potential difference (intrinsic or applied bias)
- A bridging electrolyte (high humidity or local condensation)
- Dissolved conductive species (ionic contamination)

The potential difference is the basic driving force for the charged species to travel between conductors, while the electrolyte provides the medium or path, in which the motion takes place. Ionic contamination will increase the ability of the electrolyte to lead current. Degradation of the electronic components will – if not prevented - in time often have detrimental effects on the signal transmission in the circuit, causing alteration or termination of the electric signal and ultimately failure of the device.

When taking precautions to decrease corrosion in electronics it is therefore important to minimize the contribution from any of the factors given in figure 2. In this regard the contamination control is the most feasible approach and lowering contamination levels will largely increase the corrosion reliability of a given product.

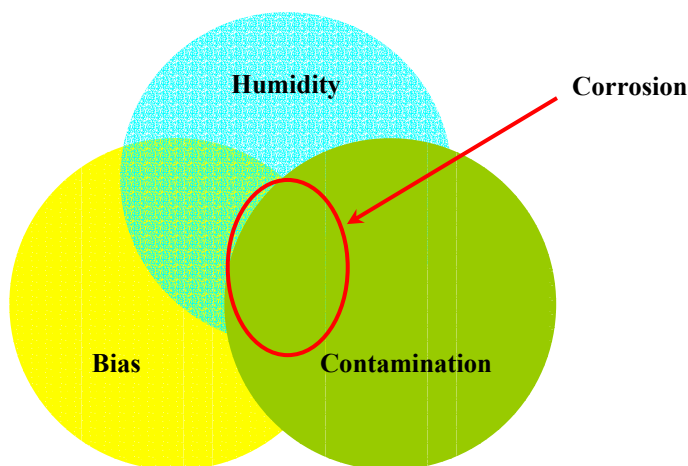


Figure 2: Combination of factors accelerates corrosion.

Residues and contamination of electronics acting as corrosion accelerators

Production related contamination can be present on any electronic device due to chemical compounds contained in the bare printed circuit board (PCB) substrate or compounds resulting from various processes during PCB manufacturing. The PCB laminate itself often contains chemical compounds like flame retardants and polymer curing agents, and PCB manufacturing involves several chemical processing steps such as electrochemical or electroless plating and etching/stripping of metal-layers or application of photoresist. Also drilling of vias and through-holes are steps in a manufacturing process that can leave different kinds of chemical residues on the PCB surface. Such residues can themselves be corrosive, or they can react with moisture from the environment to create electrolytes.

During the subsequent assembly-process, the main source of contamination is the solder flux residues in its original or decomposed form and contaminants carried by incoming components. Flux residues are one of the most common and harmful residue sources that affect the reliability of PCB assemblies, and field failures regularly occur due to flux residues that have not been activated properly or not removed during assembly. The most common flux residues are the activating species such as chloride and weak organic acids, but also additives and surfactants like polyglycols are found to reside and create problems in electronic assemblies (4,5).

Incorrect human handling of PCBs can also occur during production, and this is likewise a potential source of contamination resulting from fingerprints, skin oils, saliva, dandruff etc. Especially fingerprints (containing chlorides, amino acids etc.) can be an accelerator of electronic corrosion. Therefore, each step in the PCB manufacturing process can be a potential source for contamination if care is not taken. An overview of some of the most common contaminants originating from the production of electronic assemblies if quality control is not assured is given in figure 3.

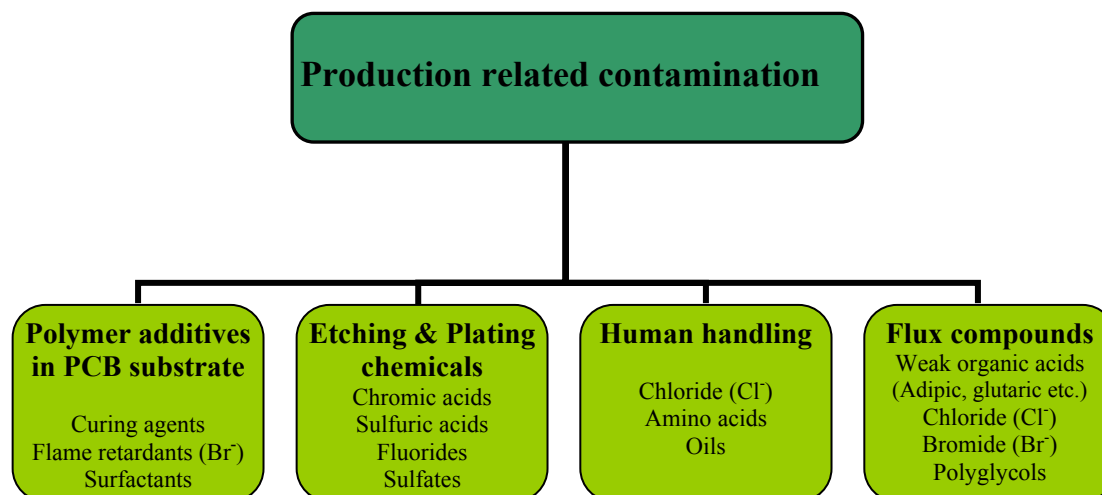


Figure 3: Overview of some common contamination sources and contaminants in PCB manufacturing (5,6,7,8,9).

The use of electronic devices in recent years has brought with it an increase in potential contamination sources, to which the assemblies can be exposed to during its application. Types and amounts of environmentally induced residues vary considerably with location. Field-environments near the sea or in tropic countries will deviate from those found inland or in arctic areas. As will the environments in highly industrial polluted locations/cities deviate from pristine nature or country-sides, and the aggressiveness and corrosivity of the user environment will vary accordingly. An overview of service related contamination is given in figure 4.

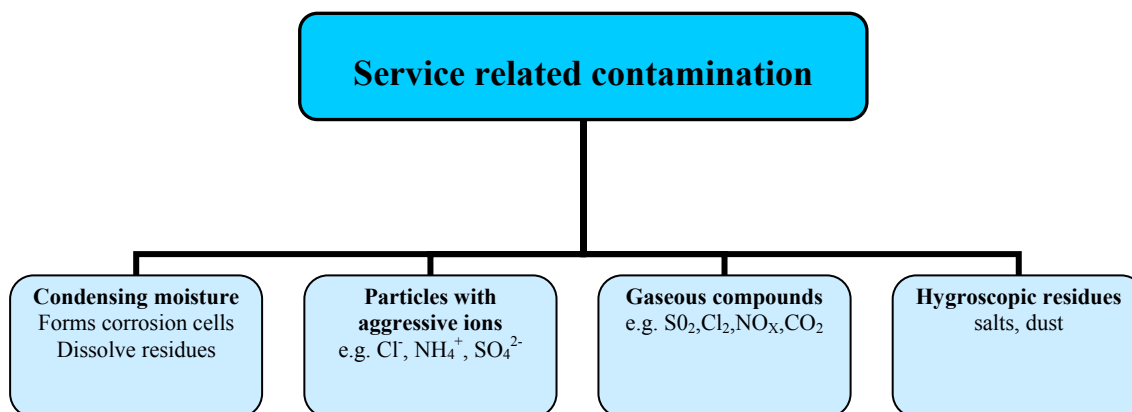


Figure 4 Overview of commonly found contaminants originating from the user environment (6,7,9,10).

Condensation of moisture on a surface will occur, when a critical RH threshold value for the specific surface is reached. For clean non-hydrophilic surfaces this value will be almost 100% RH, but for contaminated surfaces it can be much less, because hygroscopic substances will act as moisture trapping agents (10,11). A continuous moisture film between the biased conductors is a prerequisite for corrosion, so lowering of the critical RH threshold value through the presence of hygroscopic contamination will highly

increase the susceptibility of corrosion-induced failure by increasing the susceptibility of moisture condensation.

Contamination types investigated in this work

This paper shows the results of climatic testing of an industrially used electronic device deliberately contaminated at selected locations on a specific PCBA. The device consists of several PCBA's where most of them are made by lead free reflow SMD component assembling and only a few by wavesoldering. The reflow soldering involves automatic screening of solder paste, automatic pick'n'place of components or pin in paste of connectors and then heating in a standard oven in a nitrogen atmosphere for soldering.

The most miniaturized PCBA in the device is considered to be most prone to corrosion, since it has the highest bias and lowest spacing between components ratio. The effect of humidity, finger print contamination, dust, and bromide ions are investigated in detail. It has previously been mentioned that high humidity and temperature cycling can cause condensation inside the cabinet of any electronic device increasing the risk of corrosion and leakage currents. In order to investigate the effect of dust from service life, an artificial dust type was applied to the PCBA before testing. Each side of the PCBA holds approximately 0.2 g of the dust mixture. The composition of the dust mixture tested is given in Table I and has been reported to be an aggressive dust mixture (10).

TABLE I. Composition of aggressive dust mixture

Component	Wt. %
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (talc)	66
$(\text{NH}_4)_2\text{SO}_4$	29
$(\text{NH}_4)\text{HSO}_4$	3
NaHCO_3	1
KCl	1

Such ionic contaminations left on the PCBA easily dissolves into the water layer under local condensing and generates an aggressive corrosion medium by increasing the electrical conductivity of the moisture and/or by dissolving protective metal-oxide layers to promote corrosion. Furthermore the ionic contamination is often present in the form of inorganic salts, which are of a hygroscopic nature and will decrease the critical humidity of the surface for condensation. The most common ionic contaminants encountered in service life are chlorides (Cl^-), sulfates (SO_4^-), bromides (Br^-), potassium (K^+), sodium (Na^+), ammonium ions (NH_4^+) and weak organic acids (R-COO^-), but also gaseous compounds like CO_2 can dissolve as ions in local condensing areas.

The effect of bromide ions are investigated since bromide can be present on a PCBA due to the manufacturing process of laminates as well as from fluxing. For the device tested in this work, a non-halide flux system has been used so flux will not be a potential source of bromide ions in this case. Nevertheless the higher temperature when producing lead free PCBAs can have a potential risk of bromide ions to be released, since the laminate contains TBBA as a flame retardant. TBBA has been proven to decompose at temperatures as low as 250 °C with HBr as a substantial decomposition component (12). In this work the effect of bromide was investigated using a 250 ppm KBr solution as the source for bromide. For this purpose 100 μl KBr was applied to a localized area and the solution left to evaporate. Also devices with fingerprints added purposely on the PCBA surface at several locations were tested. For each experiment a separate PCBA was used.

Climatic testing results

A wide range of standards for climatic testing of electronics exists when investigating the effect of temperature, humidity, gases, salt fog, fungus, sand, dust etc. A few examples are *IEC 61189-3 (1997-04)*: Test methods for electrical materials, interconnection structures and assemblies, *ASTM B845-97*: Standard guide for mixed flowing gas (MFG) tests for electronic contacts, *ISO 9227: (2006)* Corrosion tests in artificial atmospheres - salt spray tests, *IEC 60068-2-68 (1994-08)* Environmental testing dust and sand or *ISA-S71.04-1985*: Environmental conditions for process measurements and control system: Airborne Contaminants. In this work the intent was to investigate the effect of contaminants more than to perform standardized certification of the device, therefore self-designed test methods were used (Table II).

TABLE II. Overview of test methods used for investigation of contaminants effect on corrosion of electronics.

Test Method No.	Test details	Tested
1.Humidity build-up	10 cycles of 25 hours / cycle. •17 hours off, at 95%RH, with temperature cycling from 25°C to 65°C. •8 hours of powered operation at 25°C and 95%RH. Total time 10 days.	Whole device
2.Spray test	Spraying DI water with an atomizer bottle on the biased PCBA from a distance of 20 cm. A spray of DI water covering the whole PCBA surface every 3 minutes for total of 21 minutes.	Most corrosion prone PCBA in device
3.Condensation	Immediately transferring the unbiased PCBA from 0°C, 25 % RH to 65°C, 95 % RH. Then biased for 15 minutes. 4 cycles repeated. Total time 2 hours.	Most corrosion prone PCBA in device

Whole device testing

Using test method No. 1 the whole device was mounted as a test rig inside a climatic chamber. The purpose of the initial 16 hours is to cause condensation inside the closed cabinet of the device. After a relaxation period of 1 hour the bias is turned on

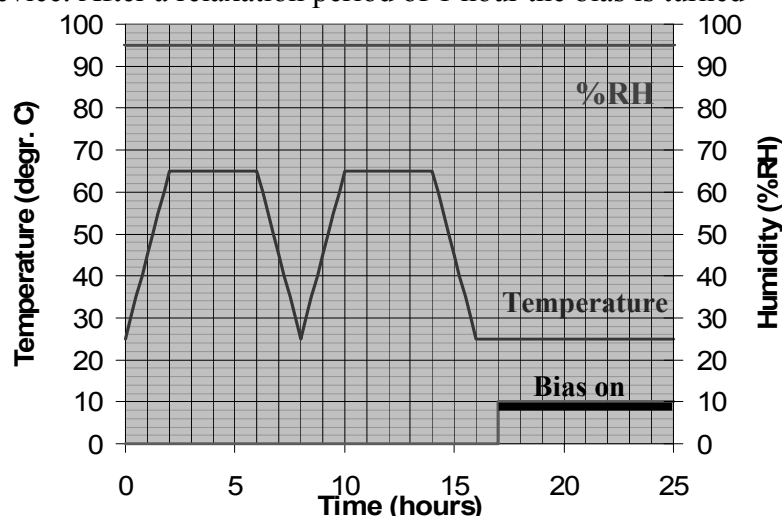
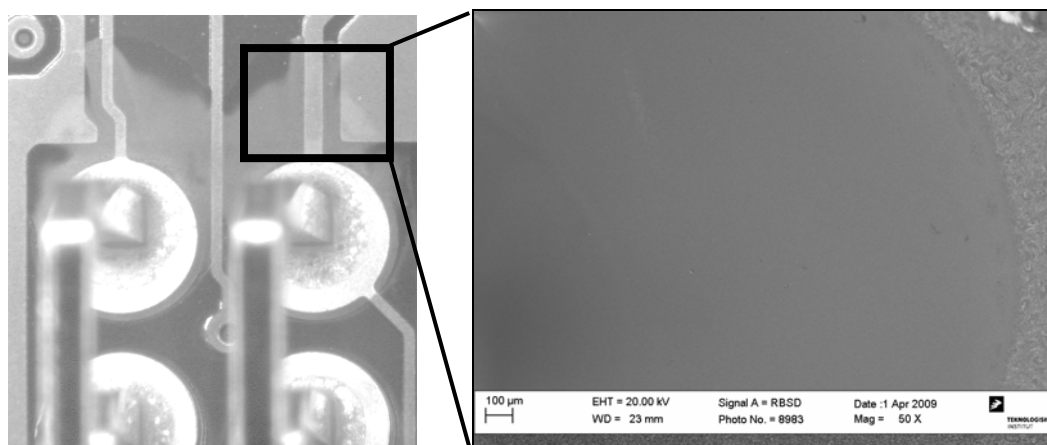
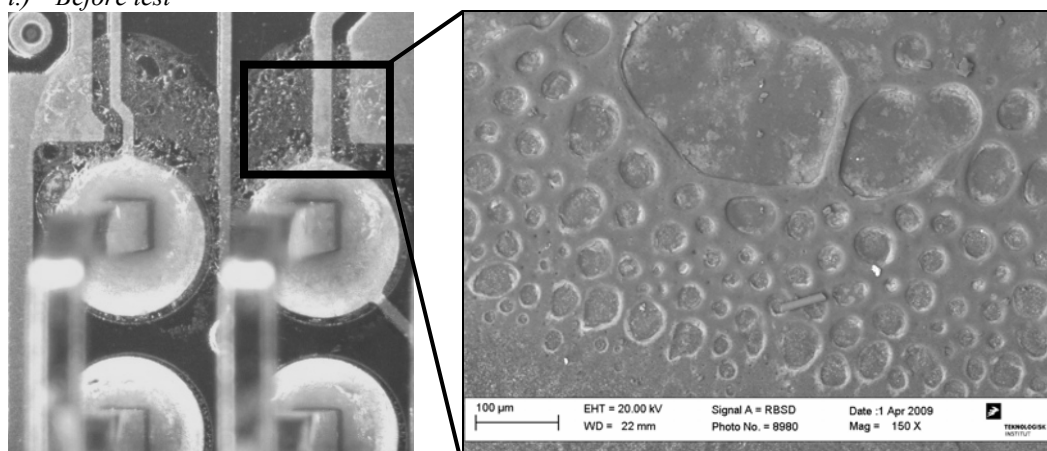


Figure 5 Temperature and relative humidity profile of device level test method No.1.

After completion of test No.1 (approximately 10 days) visible swelling of flux residues were seen. Especially blistering of the flux residue around the pin in paste component was seen as shown in figure 6.



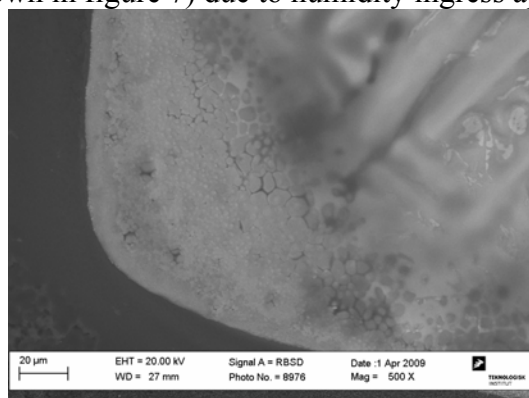
i.) Before test



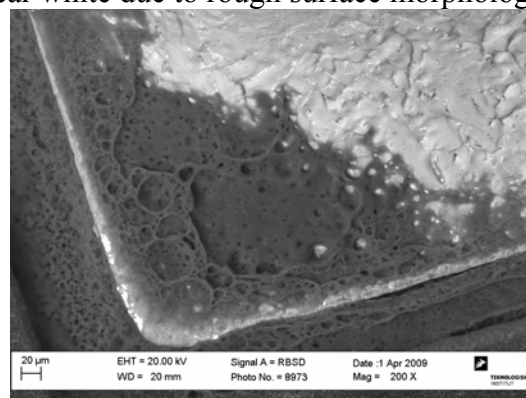
ii.) After test

Figure 6. Blistering of flux residue after climatic testing No. 1 i.) before test and ii.) after test method No.1.

When examining the flux residues with the naked eye, the blistered flux (SEM images of shown in figure 7) due to humidity ingress appear white due to rough surface morphology.



i.) Before test



ii.) After test

Figure 7. SEM images of swollen flux residue on solder pads for component assembling, after climatic testing No. 1.

The risk of swollen or blistering flux acting as a corrosion accelerator depends on the activity of flux. This has been studied in detail for a wave solder flux (13) (figure 8).

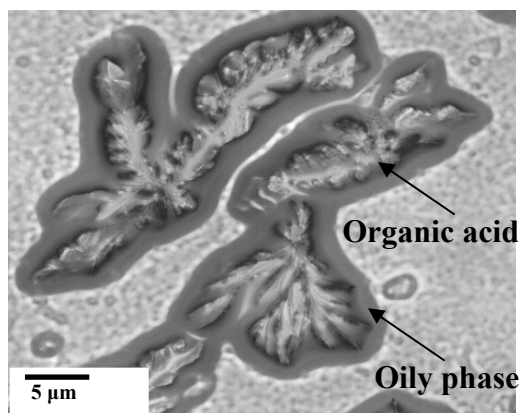


Figure 8. Light optical micrograph of active wave solder flux. The flux has not been heated, but left for evaporation at ambient for 2 hours. The solvent has evaporated and left organic acids embedded in oily phase.

The light optical micrograph of active flux reveals that mainly two components exist in the residues at all temperatures, namely the acid component, which is seen as needle-shaped crystals, and the resin oil covering the crystals. The amounts of both components are found to decrease with increasing heating temperature (figure 9).

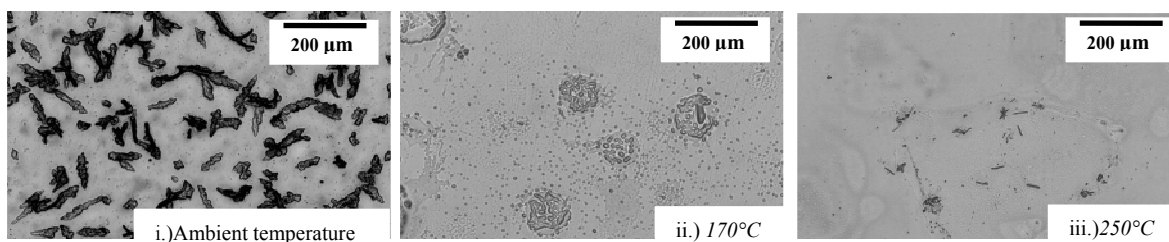


Figure 9. Morphology of flux residue on a glass plate formed after heating to various temperatures for 45 seconds.

It can be seen that the amount of flux residue decreases with increase in temperature, however, even at 170°C and 250°C considerable amount of residue still remain on the surface. Ion chromatographic analysis showed the presence of substantial amounts of acid component in the residue formed at 170°C and 250°C (13). The presence of acid components in the residue in principle can influence the corrosion of electronic components in many ways. These are: (i) by changing the pH of condensed water layer which will modify the stability of the dissolved metal ions, (ii) increasing conductivity of the water layer so that higher leakage current between electrodes for migration, and (iii) depending on the nature of acid either it can act as an activator for corrosion or inhibitor.

For this particular device tested, the flux residues swelling did not seem to have a corrosion accelerating effect. This is due to an optimum and homogenous heating cycle leaving a minimum of corrosion accelerating species as residues. All the tested devices completed the test No.1 without failures, proving the high reliability of this device.

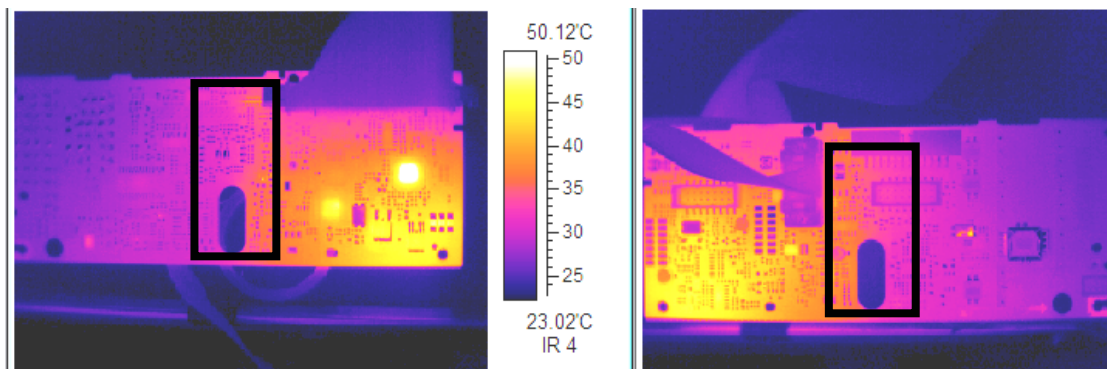
Since failure of the tested electronic device was not seen after exposure to test method No. 1, it was decided to go to even more severe test methods. For this purpose the PCBA being most prone to corrosion was isolated from the rest of the electronic device in order to avoid severe failures of high voltage PCBAs in the device due to high levels of condensation.

Test by isolating most corrosion prone PCBA of the device

The PCBA being most prone to corrosion was selected from following considerations:

- Highest bias to distance ratio
- Position in cabinet
- Thermographic behavior during biased conditions

The PCBA chosen is quite complex with a 6 layer print and more than 250 resistors, 150 capacitors, 50 transistors, and 20 IC's. The bias varies from 0-23 V, both AC and DC voltage. The PCBA is placed vertically up front in the cabinet with shielding from outside environment without being hermetically shielded. The temperature of the PCBA during running conditions reaches approximately 50 °C at some locations as shown in figure 10 by using an IR camera.



i.) Frontside with top part to the right

ii.) Backside with top part to the left

Figure 10. Thermographic image of biased PCBA, i.) fronside and ii.) backside. Black box marked region shows highest bias to distance ratio and still relatively low operating temperature region.

The thermographic image shows how especially ICs and transistors get hot during operation, because of the large currents passed during working condition of the PCBA. This heating will restrain water film formation in the top zone of the PCBA, whereas temperature of the lower end PCBA is independent of whether it is in working conditions or not. Rectangular areas shown in figure 10 are the highest bias to distance ratio area found together with relatively low operating temperature.

The effect of self heating of the biased PCBA was obvious when tested using test method No. 2, the spray test. The hot bottom part of the PCBA caused the sprayed DI water to evaporate for the first spray within minutes in this region. Both uncontaminated and contaminated PCBAs gave error messages within the 21 minute test period.

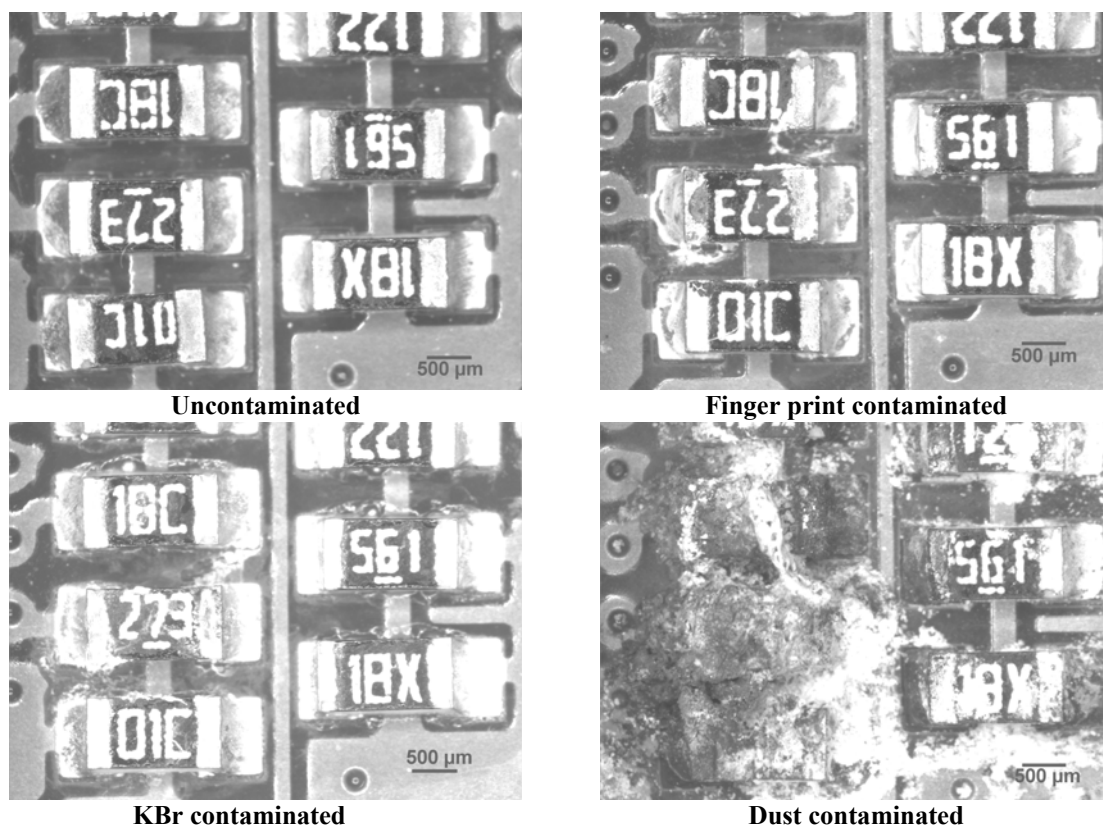


Figure 11. PCBA after 7 sprays of DI water according to test method No.2. Especially the dust contaminated PCBA showed severe corrosion.

All tests were stopped after 7 sprays and severe corrosion of especially the dusted PCBA was observed. Severe bubbling and local temperature increase on components was found for the dusted PCBA after the second spray (3 minutes). The fingerprint and KBr contaminated PCBA's both showed error codes after 6 minutes, whereas the uncontaminated lasted for 15 minutes before showing error codes. Both fingerprint and KBr contaminated regions did not show signs of severe corrosion/electrochemical migration compared to the device contaminated with dust.

In order to obtain a more controllable condensation cycle, the most prone PCBA was immediately taken from 0 °C, 25 % RH to 65 °C, 95 % RH, and immediately after exposure to humid environment the bias is turned on for 15 minutes (test method No.3). The result of this method is shown in Table III with the number of cycles for failure and the error code related to each failures.

TABLE III. Number of cycles needed for failure with different contaminants for test method 3.

Contamination type	No. of cycles to failure	Error code
Uncontaminated	4	A 38
Dust	1	No text in display
Fingerprint	1	A 13
Bromide	2	A 38

Investigation of the uncontaminated capacitors after test No.3 show sign of condensation and a fluffy white corrosion product (tin hydroxide) as shown in figure 12.

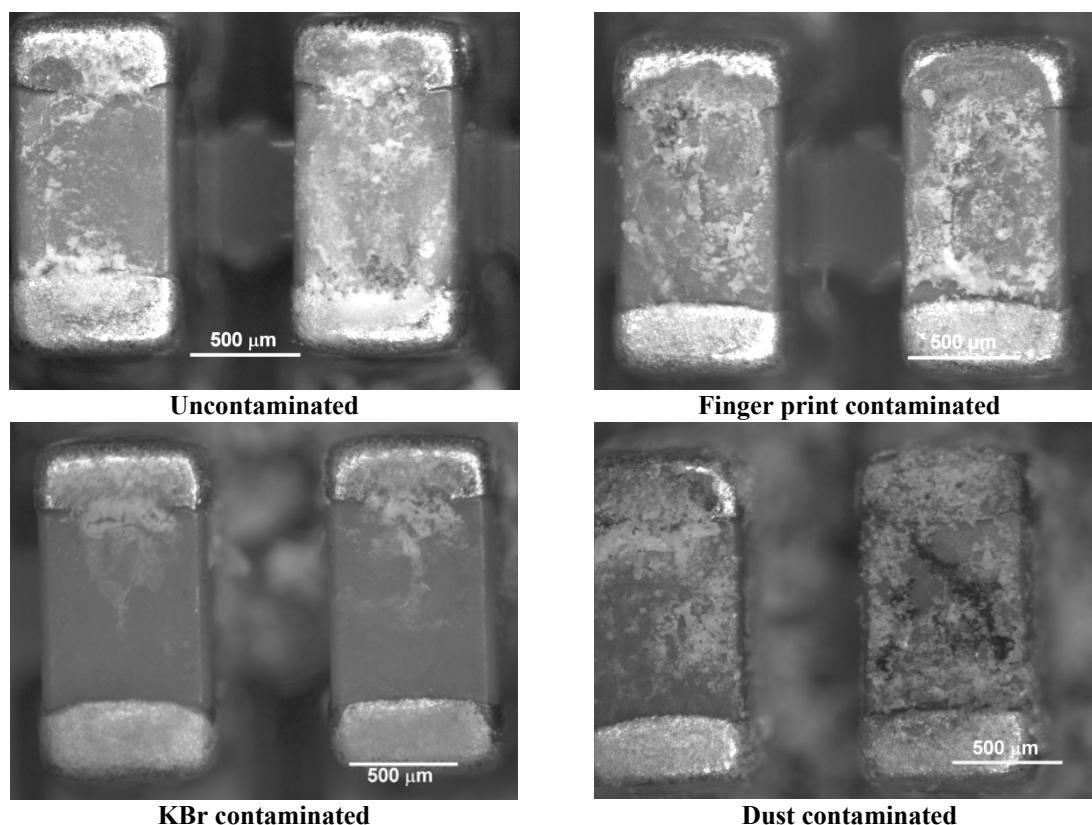


Figure 12. High resolution photographs of chip capacitors in selected region on most prone PCBA after severe condensation (test method No.3).

Both finger print and dust contaminated capacitors show the presence of metallic dendrites. The KBr contaminated capacitors have not migrated on top of the capacitors, but severe corrosion was seen at the PCBA surface in between components. This is due to the method for applying KBr using aqueous solution droplet and allowing it to evaporate causing bromide ions to have accumulated at the PCB surface more than on top of components.

Both finger print and dust contamination caused dendrite formation in some cases, just as formation of large amounts of white corrosion products (tin hydroxide) is seen. The possibility for electrochemical migration (dendrite formation) to stop depends on the lack of stability of stannate ions at the cathode areas, which is a necessary condition for the dendrite to form. If tin dissolution is high in a medium, the stability line for the formation of stannate ions in the Pourbaix diagram for tin will be moved towards more alkaline values. Under such circumstances stannate ions precipitate as tin hydroxide if the alkalization at the cathode due to electrochemical reactions is not enough to sustain the stability of stannate ions. More device level investigation is presently being carried out to understand the effect of above parameters in detail, using various concentration and aggressiveness.

Conclusion

The effect of humidity and temperature cycling was investigated by installing whole electronic devices as a test rig inside a climatic chamber. The cyclic humidity climatic test did not result in any failure or severe corrosion of the electronic device. The high humidity caused reflow flux residues to swell and blister, but since the flux residues had undergone an optimum heating cycle, no corrosion accelerating species were present in the residues and all tested electronic devices completed the test without failures.

Severe condensation was investigated using a spray test. This test clearly showed the effect of having ionic contaminants present in the form of an aggressive artificial dust on the surface. The presence of an aggressive dust mix caused severe corrosion of components and failure of the tested PCBA.

A climatic condensation cycle made it possible to distinguish between the severity of production related contaminants as finger prints, bromide ions and service life contaminants as dust showing the importance of taking precautions against such contaminants in order to decrease the risk of corrosion in electronics.

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